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(54) Title: <b>AQUEOUS DEFOAMER DISPERSIONS OF ETHYLENEBIS (STEARAMIDE)</b>			
(57) Abstract  Aqueous substantially hydrocarbon oil-free emulsions prepared from aliphatic diamides, such as ethylenebis (stearamide) (EBS) and related compounds, are found to be effective defoamers for use in various paper-making operations. These compositions avoid many of the deleterious effects of conventional oil-based EBS defoamers, thereby allowing their use on paper machines.			

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AQUEOUS DEFOAMER DISPERSIONS OF ETHYLENEBIS(STEARAMIDE)BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to substantially oil-free amide based aqueous compositions which are effective defoamers for use in paper mill operations, particularly for use on paper machines and in the presence of dilute black liquors. The term "oil" is used herein to refer to all hydrocarbon materials which are liquid at room temperature and specifically includes fluids such as mineral oils, benzene, heptane, octane, mineral seal oil, stoddard solvent, petroleum naphtha, toluene, xylene, paraffinic mineral oil, naphthenic mineral oil, and the like.

Description of the Prior Art

The problem of foam control in paper mills operations is a continuing one. Generally, it has been most effectively dealt with by using various oil-based compositions containing an alkylene diamide and/or hydrophobic silica (silicone coated silica). Oil-based amide defoamers contain a minimum of two ingredients: a wax with a high melting point (usually a fatty diamide) dispersed in a liquid hydrocarbon oil carrier, c.f. U.S. Patent No. 3,677,963. The most commonly used diamide is ethylenebis(stearamide), but other diamides or mixtures of diamides can also be found in defoamer blends. Typically, the weight fraction of diamides is between 4 and 12% whereas the weight fraction of the hydrocarbon oil is well over 80%. The oil carrier varies in composition from one defoamer to another but generally consists of a low viscosity mineral oil with paraffinic or cycloparaffinic hydrocarbons. In addition to the diamides and oil, the blends may also contain other agents such as hydrophobic silica and silicone oil, various emulsifiers and stabilizers, but these constituents generally comprise less than 10% of the formulation. U.S. Patent No. 3,723,342, for instance, discloses a defoamer composition containing 4 to 12% EBS, a surfactant, a silicone oil, and a low viscosity mineral oil. U.S. Patent No. 4,032,473 discloses an aqueous emulsion of a dispersed phase containing a liquid hydrocarbon,

EBS, hydrophobic silica particles, and a nonionic emulsifier. U.S. Patent No. 4,225,456 discloses a water-in-oil emulsion defoamer composition containing quickchilled EBS, silica, a water-soluble polymer, an emulsifier, oil and water.

While these and other similar compositions are effective defoamers for brown stock washers in pulp mills, they have recently been suspected of contributing to deposition problems in various locations in paper mills. (Dorris et al. "Analysis of Amide Defoamers in Kraft Mill Pitch Deposits," J.Pulp & Paper Science, 11:5, J149-J154, September 1985.) And recently there has been evidence that they are an indirect source of the 2,3,7,8-tetrachlorodibenzop-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) produced in kraft bleach plants. (Allen et al. manuscript distributed at the 8th International Symposium on Chlorinated Dioxins and Related Compounds, Umea, Sweden, August 21-26, 1988.) In addition, due to the large oil content, i.e. generally at least about 20 wt % but more commonly at least about 75 wt %, they have not been found useful on paper machines because they are not able to completely disperse in water and thus they cause deposits and/or oil spots on the paper being produced.

U.S. Patent No. 3,652,453 discloses bis(stearamide)-based defoamer compositions which utilizes the bis(stearamide) in the form of a "quick-chilled amide" which is prepared by using a "liquid hydrocarbon vehicle" such as benzene, toluene, heptane, octane, mineral oil, and the like. These liquid hydrocarbon vehicles are oils, as defined herein. In the defoamer compositions produced in the eight '453 Examples, one or more oils is present in an amount ranging from a low of about 85.3 wt % to a high of about 95.55 wt % of the final defoamer compositions.

Alternative oil-based defoamers have been prepared from a wide variety of chemicals. For example, U.S. Pat. No. 3,751,373 and 3,935,121 disclose defoamers based upon a combination of a fatty acid or alcohol, a polyethylene glycol mono or di ester of a fatty acid, a petroleum sulfonic acid, and 65-98% organic

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liquid. One example of a commercial aqueous defoamer is an aqueous emulsion of fatty alcohols - although it does not contain any oil phase, it does contain high melting waxes which are known to interfere with certain later processing steps. These defoamers are generally not as effective as those containing EBS and its homologues, but also do not cause the spotting problem on paper machines.

Therefore there is a need for a defoamer composition which utilizes EBS and/or other diamides, since they are such effective defoamers, while minimizing the oil content or more preferably excluding the presence of any oil from the compositions. It is an object of the present invention to produce such defoamer compositions and to utilize them in paper-making operations.

#### SUMMARY OF THE INVENTION

The present invention is a substantially oil-free aqueous defoamer composition which comprises an aliphatic diamide, an amphipathic liquid, and water. The defoamer composition is prepared by heating the aliphatic diamide to above its melting point in the presence of the amphipathic liquid and then adding that mixture to the water. A uniform dispersion/emulsion of the aliphatic diamide in water is produced and this dispersion/emulsion is an effective defoamer.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The defoamer compositions of the present invention are produced by combining an aliphatic diamide, an amphipathic liquid, and water in such a manner that a uniform dispersion of the aliphatic diamide in the water occurs while avoiding the incorporation of any substantial amounts of an oil. The term "oil" is used herein to refer to all hydrocarbon materials which are liquid at room temperature and specifically includes fluids such as mineral oils, benzene, heptane, octane, mineral seal oil, stoddard solvent, petroleum naphtha, toluene, xylene, paraffinic mineral oil, naphthenic mineral oil, and the like.

Aliphatic diamides useful in the present compositions include those obtained by reacting a polymethylene diamine containing from 2 to about 6 methylene groups with a fatty acid, i.e. a long chain aliphatic carboxylic acid having about 10 to about 22 carbon atoms in the chain. The acid may contain straight or branched chains, may have a degree of unsaturation, and may contain cycloaliphatic rings. Such fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, behenic, lauroleic, oleic, linoleic, linolenic, etc. It is customary, but not essential, that the same acid form the amide group at each of the amine groups in the polymethylenediamine. Aliphatic diamides based on fatty acids having about 16 to about 18 carbon atoms are preferred. A particularly preferred fatty acid diamide is the diamide formed from stearic acid and ethylene diamine, i.e. N,N'-ethylene bis(stearamide), hereafter referred to as EBS.

Amphipathic liquids useful in the present invention are those liquids having a sufficient amount and balance of both polar and nonpolar groups so as to enable the aliphatic diamide component to remain in suspension when added to water. The amphipathic liquid provides sufficient wetting to the surfaces of the aliphatic diamide particles to allow them to remain dispersed when added to the water. Classes of suitable amphipathic liquids useful herein include polyethylene glycol mono and di esters of fatty acids wherein the polyethylene glycol has a molecular weight of at least 300 and the fatty acids have about 14 to about 22 carbon atoms, petroleum sulfonates, and straight and branched chain alcohols having about 10 to 14 carbon atoms and reacted with an amount of ethylene oxide sufficient to produce a stable dispersion. Examples of specific amphipathic liquids useful herein include polyethylene glycol (400) monooleate, polyethylene glycol (600) dioleate, sodium petroleum sulfonate, and dodecyl alcohol reacted with 4 to 6 moles of ethylene oxide.

In addition to the aliphatic diamides and the amphipathic liquid, the defoamer compositions of this invention may further

contain small amounts of one or more oil-soluble non-ionic surfactants and/or polymers to improve the efficiency of the defoamer compositions. The non-ionic oil-soluble surfactants have been used with oil-based diamide defoamers as spreading agents. Examples of suitable non-ionic materials include condensation products of higher fatty alcohols with ethylene oxide, condensation products of alkyl phenols with ethylene oxide, condensation products of fatty acid amides with ethylene oxide, polyethylene glycol esters of long chain fatty acids, ethylene oxide condensation products of polyhydric alcohol partial higher fatty acid esters and their inner anhydrides, long chain polyglycols in which one hydroxyl group is esterified with a higher fatty acid and the other hydroxyl group is etherified with a low molecular weight alcohol, propylene glycol mono and di lower esters and ethers, ethylene oxide-propylene oxide block copolymers, vinyl acetate based copolymers such as Paratone 440 of Exxon Chemical, esters of ethylene oxide-propylene oxide block copolymers, polybutenes, ethylene-propylene rubbers, and the like. Preferably, these compounds will be used in mixtures to obtain optimum properties for a particular defoamer composition for a particular end use. Routine experimentation will determine the specific non-ionic oil-soluble materials to be used for a particular application. These materials, if present, will generally represent less than about 5, preferably less than about 3, wt % of the final composition.

Although preferably no oil is present in the defoamer compositions of this invention, the incorporation of small amounts thereof generally as a carrier for the non-ionic oil-soluble materials has not been found detrimental. The compositions thus even though they may contain up to about 3 wt %, preferably up to about 1 wt %, oil are substantially oil-free as compared to prior art bis(stearamide) defoamer compositions which contain at least 20 wt % oil and more commonly about 80 to 95 wt % oil.

Furthermore, the compositions may also contain other conventional defoamer additives such as hydrophobic silica, anionic and cationic surfactants, waxes, fatty alcohols, and fatty acids. The other materials, if present, will normally represent less than about 3 weight % of the total defoamer compositions.

Generally the aliphatic diamides will be used in amounts ranging from about 1 to 15, preferably about 2 to about 10, weight % of the defoamer composition. The amphipathic liquid will generally be used in an amount of about 10 to about 35, preferably about 15 to about 30, and most preferably about 17 to about 25, weight %. The non-ionic oil-soluble surfactants and polymers will be used in amounts up to a total of about 5 weight %. The balance of the compositions will be water. For ready incorporation into currently used defoamer equipment, the defoamer compositions will generally have a viscosity of about 1,000 to about 2,500 centipoise as determined by a Brookfield RVT viscometer using spindle number 3 at 50 rpm.

To prepare the defoamer compositions, the aliphatic diamide is heated to above its melting point in the presence of the amphipathic liquid. The heating continues with routine stirring until the diamide has completely dissolved. The diamide-amphipathic liquid solution is then poured into stirred water and stirring is continued until a smooth creamy white dispersion is obtained, i.e. for a few hours or even overnight. The water will generally be at about room temperature when the diamide solution is added to it, but this has not been found to be critical. The diamide solution may be added either hot or after it has cooled to room temperature. The non-ionic oil-soluble materials, if used, may be added either to the diamide solution before its addition to the water or to the final dispersion with additional stirring.

The substantially oil-free defoamer compositions of this invention have particular utility in controlling foam, i.e. inhibiting foam formation and destroying existing foam, in a



variety of pulp and paper mill operations. Generally, these defoamers will find primary use in treating foams that could previously not be treated with diamide defoamers due to the deposit problem referred to above. The defoamer compositions are especially useful for controlling foam which occurs in dilute black liquors. By "dilute" is meant that the concentration of total solids in the liquid phase is generally below about 5 %, preferably below about 2 %, and most preferably below about 1 %, all by weight. As such they may be used in controlling foam in screen rooms, on paper machines, in paper coatings, and to treat the plant effluent which is going to a waste treatment facility.

The defoamer composition may be added to the system neat, or it may be prediluted or it may be added on the fly. Since the present defoamer compositions are completely water-dispersible, they may be handled in like manner to other water-based defoamers, even though they contain aliphatic diamides.

The quantity of the defoamer compositions required to control foam will obviously vary depending upon the specific nature of the liquid to be treated and upon the individual components used to prepare the defoamers. Generally, however, a quantity of defoamer from about 0.5 to 3 pounds per ton of pulp will be suitable, preferably about 1 to about 2 pounds.

The following examples are presented for purposes of illustration and not limitation. All parts and percents are by weight unless otherwise specified.

#### EXAMPLE I

A mixture of 1.0 g ethylenebis(stearamide) and 24.0 g polyethylene glycol (600) di-oleate is stirred and heated to approximately 140 C. When all of the EBS has dissolved, the hot solution is poured slowly into 75.0 g well-stirred room-temperature water. The temperature of the resulting dispersion is about 40 C. It is inhomogeneous, i.e. lumpy, but becomes smooth and homogeneous with continued stirring. The resulting

dispersion is stable and does not separate upon standing over a period of three weeks.

#### EXAMPLE II

The procedure of Example I is repeated to produce 5 gallons of a defoamer composition which contains 3% ethylenebis-(stearamide), 22% polyethylene glycol (600) dioleate, and 75% water.

To evaluate the defoaming ability of the composition, a test is performed in the screen room of a paper mill. In the test, the addition of the defoamer is controlled by a computer which reads information on the height of the foam in the system. The defoamer is added at a constant rate, and when the foam level reaches or exceeds a preset level, the speed of the defoamer pump is increased to add more defoamer until the foam level drops below the preset level. Then the pump speed is reduced to its original setting. The performance of the defoamer is determined by calculating the pounds of defoamer used per minute of operation.

In this test, 31.31 pounds of the defoamer composition is used in 21 minutes of operation. At no point during the test does the foam exceed the preset level. The efficiency of the defoamer is therefore 1.49 pounds per minute. The commercially used defoamer at this plant is Discotech 5543 from Callaway Chemical and it is used in the screen room at a rate ranging from about 1.43 to about 1.70 pounds per minute. Thus the defoamer of this example is equivalent in performance to the commercial product.

#### EXAMPLE III

The procedure of Example II is repeated with a variety of defoamer compositions within the scope of this invention. The respective formulations and efficiencies are provided in Tables A and B below. As can be seen, the defoamers of the present invention are consistently superior to the commercial defoamer now used at this plant. Since, in no case with the present

defoamers did the foam exceed the mill's preset level, the amount of defoamer actually required for this use is below these amounts.

TABLE A  
Formulations of Example III

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
EBS	3	3	3	3	3	3	3	3	3
PEGDO (1)	21	21	20		21	20	21	20	20
Water	75	75	75	75	75	75	75	75	75
VAc (2)	1		1				1	1	
PPGMBE (3)		1	1			1			1
SPS (4)				22					
DOEEO/PO (5)					1	1			
EO/PO (6)							1	1	1

- (1) PEGDO is polyethylene glycol (600) di-oleate  
 (2) VAc is an oil-soluble vinyl acetate-based copolymer  
 (3) PPGMBE is polypropylene glycol monobutyl ether  
 (4) SPS is sodium petroleum sulfonate  
 (5) DOEEO/PO is a di-oleate ester of an ethylene oxide/propylene oxide block copolymer  
 (6) EO/PO is an ethylene oxide/propylene oxide block copolymer

TABLE B  
Results of Example III

<u>Sample</u>	<u>Lbs.Used</u>	<u>Time(min.)</u>	<u>Lbs./Min.</u>
A	37.52	26	1.44
B	33.68	25.75	1.31
C	35.54	30	1.18
D	34.22	51.5	0.66
E	35.98	43.5	0.83
F	34.88	31	1.13
G	35.54	27	1.32
H	35	28.75	1.22
I	35.98	26	1.38

#### EXAMPLE IV

The procedure of Example I is repeated to produce a defoamer composition containing 4% EBS, 19% polyethylene glycol (400) monooleate, 75% water, 1% oil-soluble vinyl acetate-based copolymer in mineral oil (Paratone 440 of Exxon Chemical which contains about 30% copolymer), and 1% ethylene oxide/propylene oxide block copolymer. The composition contains about 0.7% oil.

To evaluate the performance of this composition at defoaming on a paper machine, the above composition is substituted directly for the commercial fatty alcohol-based defoamer on a paper machine. The grade of paper being produced is unbleached linerboard. The defoamer is added without prior dilution to both the headbox and the wire pit. During a trial with a total of five gallons of the defoamer composition, the usage was at a rate of 1.5 pounds per ton of dry paperboard produced. In this plant, the commercial fatty alcohol-based defoamer is normally used at a rate of 2 lbs./ton of dry paperboard.

The defoamer composition is more effective than the commercial defoamer customarily used and leaves no deposits on either the paper or the machine.

#### EXAMPLE V

The procedure of Example I is repeated using a variety of different amphipathic liquids to dissolve the EBS. The compositions contain 3 parts EBS, 22 parts amphipathic liquid, and 75 parts water. The following results, wherein EO stands for ethylene oxide, are observed:

<u>Amphipathic Liquid</u>	<u>Stable Dispersion?</u>
Dodecyl alcohol - 2 moles EO	No
Dodecyl alcohol - 3 moles EO	No
Dodecyl alcohol - 4 moles EO	Yes
Dodecyl alcohol - 5 moles EO	Yes
Dodecyl alcohol - 6 moles EO	Yes
Dodecyl alcohol - 7 moles EO	No
Dodecyl alcohol - 9 moles EO	No
Polypropylene glycol (700) distearate	No
Polyethylene glycol (200) dioleate	No
Polyethylene glycol (400) monooleate	Yes

EXAMPLE VI

The procedure of Example I is repeated except that the EBS solution is cooled to room temperature before it is added to the water. The resultant dispersion is as stable as that of Example I showing that the rapid cooling provided by the water is not required to produce the defoamers of this invention.

EXAMPLE VII

The procedure of Example II is repeated to produce two compositions for extended testing in the screen room. The compositions both contain 3% EBS, 19% polyethylene glycol (600) dioleate, 75% water, 1% oil-soluble vinyl acetate-based copolymer, 1% polypropylene glycol monobutyl ether, and 1% ethylene oxide - propylene oxide block copolymer. They differ only in when the three 1% additions are made - in the first case ("before") they are added to the hot EBS solution before its addition to the water, while in the other ("after") they are added after the addition to water. The two compositions are evaluated versus the commercial defoamer and the results are:

<u>Sample</u>	<u>Lbs.Used</u>	<u>Time(min.)</u>	<u>Lbs./Min.</u>
Before	72.38	77.75	0.93
After	74.15	68	1.09
Commercial	45	25	1.80

Thus, the compositions of the present invention are substantially improved defoamers as compared to the commercial product currently in use at this paper mill. No substantial difference is seen based upon when the minor additions are made.

CLAIMS:

1. A substantially oil-free aqueous defoamer dispersion composition which comprises an aliphatic diamide, an amphipathic liquid having a sufficient amount and balance of both polar and nonpolar groups so as to enable the aliphatic diamide to remain in suspension when added to water, and water.

2. The defoamer dispersion composition of Claim 1 wherein the aliphatic diamide is obtained by reacting a polymethylene diamine containing from 2 to about 6 methylene groups with a fatty acid having about 10 to about 22 carbon atoms in the chain.

3. The defoamer dispersion composition of Claim 2 wherein the fatty acid is selected from the group consisting essentially of capric, lauric, myristic, palmitic, stearic, arachidic, behenic, lauroleic, oleic, linoleic, and linolenic acids.

4. The defoamer dispersion composition of Claim 2 wherein the fatty acid has about 16 to about 18 carbon atoms.

5. The defoamer dispersion composition of Claim 1 wherein the diamide is N,N'-ethylenebis(stearamide) which is formed from stearic acid and ethylene diamine.

6. The defoamer dispersion composition of Claim 1 wherein the amphipathic liquid is selected from polyethylene glycol mono- and di- esters of fatty acids wherein the polyethylene glycol has a molecular weight of at least 300 and the fatty acids have about 14 to about 22 carbon atoms, petroleum sulfonates, and straight and branched chain alcohols having about 10 to 14 carbon atoms and reacted with an amount of ethylene oxide sufficient to produce a stable dispersion.

7. The defoamer dispersion composition of Claim 6 wherein the amphipathic liquid is selected from the group consisting of polyethylene glycol (400) monooleate, polyethylene glycol (600)

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dioleate, sodium petroleum sulfonate, and dodecyl alcohol reacted with 4 to 6 moles of ethylene oxide.

8. The defoamer dispersion composition of Claim 1 which comprises about 1 to about 15 weight % aliphatic diamide, about 10 to about 35 weight % amphipathic liquid, and the balance water.

9. The defoamer dispersion composition of Claim 1 which comprises about 2 to about 10 weight % aliphatic diamide, about 17 to about 25 weight % amphipathic liquid, and the balance water.

10. The defoamer dispersion composition of Claim 1 wherein it has a viscosity of about 1,000 to about 2,500 centipoise as determined by a Brookfield RVT Viscometer using spindle no. 3 at 50 rpm.

11. The defoamer dispersion composition of Claim 1 further containing up to about 5 weight percent of an oil-soluble nonionic material selected from the group consisting of surfactants and polymers.

12. The defoamer dispersion composition of Claim 11 wherein the oil-soluble non-ionic material further comprises an oil carrier.

13. The defoamer dispersion composition of Claim 1 wherein the oil content is less than about 3 weight %.

14. The defoamer dispersion composition of Claim 1 wherein the oil content is less than about 1 weight %.

15. The defoamer dispersion composition of Claim 1 wherein the oil content is about 0.

16. The defoamer dispersion composition of Claim 1 which is prepared by heating the aliphatic diamide to above its melting

point in the presence of the amphipathic liquid with stirring and then pouring the diamide-amphipathic liquid solution into stirred water with the stirring continued until a smooth creamy white dispersion is obtained.

17. The defoamer dispersion composition of Claim 16 wherein the amphipathic liquid is selected from polyethylene glycol mono- and di- esters of fatty acids wherein the polyethylene glycol has a molecular weight of at least 300 and the fatty acids have about 14 to about 22 carbon atoms, petroleum sulfonates, and straight and branched chain alcohols having about 10 to 14 carbon atoms and reacted with an amount of ethylene oxide sufficient to produce a stable dispersion.

18. The defoamer dispersion composition of Claim 16 wherein the amphipathic liquid is selected from the group consisting of polyethylene glycol (400) monooleate, polyethylene glycol (600) dioleate, sodium petroleum sulfonate, and dodecyl alcohol reacted with 4 to 6 moles of ethylene oxide.

19. A method of controlling foam in dilute black liquors of paper mills wherein the concentration of solids in the liquid phase is below about 2 % which comprises adding thereto an amount effective for the purpose of a composition of Claim 1.

20. The method of Claim 19 wherein the composition comprises about 1 to about 15 weight % N,N'-ethylenebis (stearamide), about 10 to about 35 weight % amphipathic liquid which is selected from the group consisting of polyethylene glycol mono- and di- esters of fatty acids wherein the polyethylene glycol has a molecular weight of at least 300 daltons and the fatty acids have about 14 to about 22 carbon atoms, petroleum sulfonates, and straight and branched chain alcohols having about 10 to 14 carbon atoms and reacted with an amount of ethylene oxide sufficient to produce a stable dispersion, and the balance water.



# INTERNATIONAL SEARCH REPORT

International Application No  
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**A. CLASSIFICATION OF SUBJECT MATTER**  
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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 D21H B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 155 004 (SANDOZ) 18 September 1985 see page 2, line 48 - page 3, line 59; claims 1-26 -----	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/01952

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2155004	18-09-85	CH-A, B 673190	28-02-90
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